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Distinctive Characteristics of Carbon Tetrachloride Addition to Olefins in the Presence of Copper Complexes with Donor Ligands[1]

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Abstract—The interaction between CCl_4 and olefins with different structures is studied in the presence of copper complexes with P-, S-, and N-containing donor ligands. Kinetic and spectroscopic studies show that the ability of olefins to be coordinated to copper complexes governs the rate, the product composition, and the reaction mechanism. Depending on the olefin and the structure of the metal complex, either typical radical-chain reactions or processes without free radicals are observed.

INTRODUCTION

The reaction of CCl_4 with unsaturated compounds is a promising method for hydrocarbon functionalization. For this reaction, the radical-chain mechanism is commonly accepted. The simplest variant of this mechanism is [1, 2]

$$M + CCl_4 \longrightarrow MCl + C\dot{C}l_3 \text{ (chain initiation)},$$

$$C\dot{C}l_3 + \underset{\textbf{Ol}}{RCH_2CH{=}CHR'} \longrightarrow \underset{\textbf{R}_1^{\bullet}}{RCH_2\dot{C}HCH(R')CCl_3} \quad \text{(chain propagation)}, \qquad \text{(I)}$$

$$R_1^{\bullet} + CCl_4 \longrightarrow R_1Cl + C\dot{C}l_3 \quad \text{(chain propagation, telomerization)}, \qquad \text{(II)}$$

$$R_1^{\bullet} + Ol \longrightarrow R_2^{\bullet} \quad \text{(chain propagation, telomerization)}, \qquad \text{(III)}$$

$$R_2^{\bullet} + Ol \longrightarrow R_3^{\bullet} \longrightarrow R_i^{\bullet} \quad \text{(chain propagation, telomerization)}, \qquad \text{(IV)}$$

$$R_i^{\bullet} + CCl_4 \longrightarrow R_iCl + C\dot{C}l_3 \quad \text{(chain propagation, telomerizayion)}, \qquad \text{(V)}$$

$$2C\dot{C}l_3 \longrightarrow C_2Cl_6 \quad \text{(chain termination)}, \qquad \text{(VI)}$$

where M is the initial metal complex. A decrease in temperature resulted in the shortening of the chain length and, in the long run, in the nonchain radical mechanism.

Taking into account a decrease in the strength of the C–H bond in the allyl position relative to the multiple bond, the following reactions of chain transfer leading to the formation of chloroform and substitution products are expected:

$$C\dot{C}l_3 + RCH_2CH{=}CHR' \longrightarrow CHCl_3 + \underset{\textbf{R}_1'^{\bullet}}{R\dot{C}HCH{=}CHR'} \qquad \text{(VII)}$$

(chain propagation, substitution),

$$R_1'^{\bullet} + CCl_4 \longrightarrow R_1'Cl + C\dot{C}l_3 \qquad \text{(VIII)}$$

(chain transfer, substitution).

In most cases, metal should be preliminarily reduced by a ligand or, possibly, by an olefin to initiate the reaction. This is typical of Cu(II) complexes [3]:

$$Cu(II) + Red \longrightarrow Cu(I) + Red^{+}.$$

Here, Cu(I) and Cu(II) are the copper complexes in the corresponding oxidation states; Red and Red^+ are the reducing agent and its oxidized form. The preliminary splitting of ligand is possible, as in the initiation of the reaction by iron carbonyl complexes [4].

An alternative reaction mechanism that involves intermediate coordination complexes and occurs without the escape of free radicals into the bulk is discussed in [5, 6]. As a rule, the structure of intermediates is unknown, but more or less reasonable assumptions are made. Thus, for the addition of carbon tetrachloride to ethylene and butadiene in the presence of a binuclear iron carbonyl complex, the interaction between a trichloromethyl radical and an unsaturated compound in the coordination sphere of the complex without the rupture of the bridging bond is assumed [7]. Our recent data [8] show that the reaction mechanism and the

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products significantly depend not only on the catalyst, but on the nature of the unsaturated compound as well. For example, in the presence of Cu(I) triphenylphosphine complex, cyclohexene reacts via the radical-chain mechanism, whereas allyl chloride seems to react via the coordination mechanism and the intermediate formation of polynuclear complexes. In the reactions of carbon tetrachloride with unsaturated compounds, the composition of products and kinetics significantly depend on the direction of process development. In this paper, these circumstances are used to determine the reaction mechanism in the presence of copper complexes and elucidate the factors that are favorable for the occurrence of the reaction by one or another route.

EXPERIMENTAL

Copper triphenylphosphine (PPh_3) complexes in a molar ratio of components of 1 : 1 and 1 : 3 were prepared according to the standard procedure [8]. Supported catalysts were prepared by the impregnation of silochrom with chloroform solutions of phosphine complexes at room temperature. A catalyst containing dimethylformamide (DMF) complex of copper was obtained by impregnating silochrom with mixed DMF–chloroform solutions of $CuCl_2$.

Copper monoethanolamine (MEA) complex, which was the mixed alcoholate with the composition $(CuCl)_2(NH_2C_2H_5O)_2(NH_2C_2H_5OH)_2$, was obtained by the reaction of anhydrous Cu(I) chloride with a double molar excess of MEA in chloroform at room temperature. The precipitate was washed with ethanol and dried in a vacuum setup. The concentration of copper was determined by the titrimetric method. The complexes were identified by IR spectroscopy and thermal analysis. Organic substances were dried and distilled over P_2O_5.

CCl_4 and olefin in a molar ratio of 10 : 1 and copper complexes in concentrations from 6×10^{-3} to 8×10^{-2} mol/l were placed into glass ampules. To prepare the samples containing the copper complex of dibutyl sulfide (Bu_2S), the known amount of the ligand was condensed in a vacuum in ampules containing the reaction mixture and CuCl. Then, the ampules were sealed. The samples containing other copper complexes were prepared in air; then, the ampules were connected to the vacuum setup; dissolved gases were removed; and the ampules were sealed. The reaction was performed at 403–453 K for 0.5–8.0 h. Reaction products were analyzed by chromatography using an LKhM 3700 chromatograph with a flame-ionization detector and columns with SE-30 and Reoplex stationary phases. The compounds were identified by the Kovats retention index and by comparison with reference substances.

Electron spectra were recorded in air in the region from 800 to 300 nm using a Shimadzu UV-2101PC spectrometer.

The ESR spectra of frozen solutions were recorded in thin-wall quartz ampules using a Varian E-3 instrument.

RESULTS AND DISCUSSION

Reaction of CCl_4 with Octene-1

In the reaction of CCl_4 with octene, only two products were formed: monoadduct (1,1,1,3-tetrachlorononane) and the product of allyl substitution (monochlorinated octene). The composition of reaction products depended insignificantly on the choice of a copper complex. Some examples are presented in Table 1.

It follows from Table 1 that the extent of the reaction may be higher than 50% for 5 h, and the monoadduct was almost the sole product. Similar data were published for the benzoyl peroxide-initiated reaction of CCl_4 with the nearest analog of octene-1, heptene-1: only monoadduct was detected, and no measurable amounts of the products of substitution and radical recombination were observed [9]. Thus, the composition of products in the reaction between CCl_4 and octene does not contradict the usual mechanism of the radical-chain process mentioned above. The absence of higher telomers is explained by the excess CCl_4 and steric hindrances to the reaction between $CCl_3CH_2\dot{C}HC_6H_{13}$ radical that contains bulky substituents and a new olefin molecule.

Reaction of CCl_4 with Cyclohexene

In the reaction of CCl_4 with cyclohexene in the presence of copper complexes and a typical radical initiator (benzoyl peroxide), several products were formed: the product of addition (1-trichloromethyl-2-chlorocyclohexane), the product of allyl substitution (3-chlorocyclohexene), and the products of radical dimerization

Table 1. Yields (%) of the main products of the reaction between CCl_4 and octene-1 at different temperatures ([Cu] = 0.006 M, [Ol] = 0.7 M, [CCl_4] = 9.6 M; reaction time, 5 h)

Catalyst	Tetrachlorononane	Chlorinated octene	Tetrachlorononane	Chlorinated octene
	403 K		413 K	
$(CuClPPh_3)_4/SiO_2$	14	0.2	53	0.5
$CuCl_2DMF/SiO_2$	20	0.5	29	5.0

(hexachloroethane and the dimer of cyclohexene). In addition, chloroform and hydrogen chloride were present in the reaction mixture. The data are summarized in Table 2.

The data obtained for the reaction initiated by benzoyl peroxide were close to those reported in [10]. The products obtained in the presence of copper complexes and those obtained in the presence of benzoyl peroxide were close in composition. A relatively low yield of the recombination product of organic radicals, especially in comparison with that of the substitution product, and a higher yield of hexachloroethane were common to all heterogenized complexes. The yield of the substitution product was higher than that of the addition product. On the contrary, the rather high yields of the addition product are typical of homogeneous complexes. The qualitative agreement between the compositions of products obtained in the presence of homogeneous complexes and in the presence of benzoyl peroxide and, especially, the presence of considerable amounts of the products of the quadratic recombination of radicals allowed us to state that the process has a radical nature in all cases. At the same time, the quantitative differences observed for the reactions involving copper complexes or peroxide and for the reactions occurring in the presence of different copper complexes pointed to some other species that participated in the chain propagation, along with radicals $CCl_3^{\bullet}$, $R_1^{\bullet}$, and $R_1'^{\bullet}$ (see the reaction scheme). An increase in the yield of the substitution product and a simultaneous decrease in the yield of cyclohexene dimer in the reaction initiated with copper complexes compared to the reaction initiated with peroxide pointed to the fact that, instead of cyclohexenyl radical, a more active species reacted with CCl_4 to give the same product, 3-chlorocyclohexene. It might be assumed that the cyclohexenyl-radical complex of Cu(I) ion formed in the system or an unstable organocopper compound acted as this active species. In addition, the reaction was evidently facilitated by the formation of the chlorinated olefin complex of copper rather than free chlorinated olefin as a primary product:

$$\mathrm{CuClL}_n + \mathrm{R}_1'^{\bullet} \longrightarrow [\mathrm{CuClL}_{n-1}(\mathrm{R}_1'^{\bullet})] + \mathrm{L}, \qquad \text{(IX)}$$

$$\begin{gathered}[\mathrm{CuClL}_{n-1}(\mathrm{R}_1'^{\bullet})] + \mathrm{CCl}_4 \\ \longrightarrow \mathrm{CuClL}_{n-1}(\mathrm{R}_1'\mathrm{Cl}) + \mathrm{CCl}_3^{\bullet}.\end{gathered} \qquad \text{(X)}$$

The formation of complexes involving chlorinated olefin makes the chain transfer energetically more advantageous. In the allyl isomerization of dichlorobutenes, rather stable complexes containing Cu(I), organic ligands, and chlorinated olefins of the allyl structure were found [11]. An increase in the concentration of trichloromethyl radical generated by reactions (IX) and (X) is a plausible reason for an increase in the hexachloroethane yield. Thus, the scheme of the radical process in the description of the reaction of CCl_4 with cyclohexene should be supplemented by the above-mentioned reactions. It should be noted that, although the yields of the products in the cyclohexene–CCl_4 system can be higher than 50%, the reaction is never complete. Because the process is energetically very favorable (the heat of CCl_4 addition to a multiple bond is ~20 kcal/mol), the retardation of the reaction was not related to reaching equilibrium. The retardation of the reaction may be explained by the low activity of stable complexes formed during the generation of radicals. Another possible reason is the destruction of ligands incorporated into initial complexes. These processes will be considered below in more detail for the reaction involving allyl chloride.

A difference in the behavior of cyclohexene and acyclic alkenes (linear alkenes are much more active and form substitution products in low yields) is evidently due to the different activities of the corresponding hydrocarbons in the reaction with trichloromethyl radical. Its addition to cyclohexene was sterically hindered, and the abstraction of hydrogen accompanied by the formation of the radical of the allyl structure domi-

Table 2. Yields (%) of the products of the reaction between CCl_4 and cyclohexene at 403 K ($[Cu] = 6 \times 10^{-3}$ M, [Ol] = 0.8 M, $[CCl_4]$ = 9.6 M; reaction time, 5 h)

Catalyst	3-Chlorocyclohexene	Hexachloroethane	Dimer of cyclohexene	1-Trichloromethyl-2-chlorocyclohexane
$CuCl_2DMF/SiO_2$	6.0	2.2	2.0	3.0
$[CuClPPh_3]_4/SiO_2$	6.0	2.8	1.4	1.0
$CuCl(MEA)_2/SiO_2$	15.0	Traces	4.0	14.0
$CuClBu_2S$ (homogeneous)	0.8	0.4	Traces	2.5
Benzoyl peroxide (0.1 M)	3.2	0.2	8.0	7.0

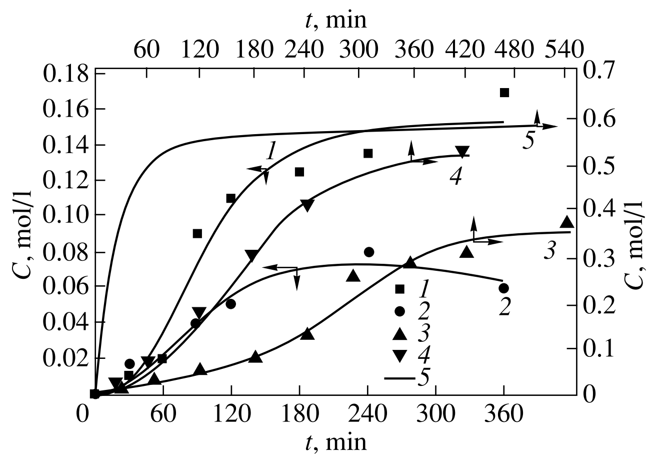

Fig. 1. Accumulation curves for the products of the reaction of CCl_4 with (*1–4*) allyl chloride and (*5*) cyclohexene [14]: for (*1*) pentachlorobutane and (*2*) trichlorobutene in the presence of CuCl and Bu_2S ([Cu] = 0.08 M, $[Bu_2S]$ = 0.15 M); for pentachlorobutane in the presence of (*3*) $CuCl(PPh_3)_3$ and (*4*) $[CuClPPh_3]_4$; for (*5*) trichloromethylchlorocyclohexane in the presence of $[CuClPPh_3]_4$ ([Cu] = 0.08 M, [Ol] = 0.9 M, $[CCl_4]$ = 9.6 M).

nated. The formation of some amounts of chlorinated octene in the reaction of octene-1 initiated by copper complexes may be explained by a small contribution from processes (IX) and (X).

Reaction of CCl_4 with Allyl Chloride

It was mentioned above that the formation of complexes between copper chloride and chlorinated olefins of the allyl structure may have a significant effect on the process. From this viewpoint, allyl chloride, which forms rather stable polynuclear complexes with copper ions [12], is of interest. Earlier [8], we found that the reaction of CCl_4 with allyl chloride in the presence of copper triphenylphosphine complexes yielded two products, the adduct (1,1,1,3,4-pentachlorobutane) (**I**) and 4,4,4,-trichlorobutene-1 (**II**):

$$2\mathrm{CH_2Cl{-}CH{=}CH_2} + 2\mathrm{CCl_4} \longrightarrow \underset{\mathbf{I}}{\mathrm{CH_2Cl{-}CHCl{-}CH_2{-}CCl_3}} + \underset{\mathbf{II}}{\mathrm{CH_2{=}CH{-}CH_2{-}CCl_3}}.$$

The formation of compound **II**, which may result from the recombination of allyl and trichloromethyl radicals in the coordination sphere of the oxidized metal complex, made it possible to assume an unusual mechanism conventionally called the “coordination mechanism” for the reaction of CCl_4 with allyl chloride. Note that compound **II** was not formed in the presence of benzoyl peroxide, which is a typical radical initiator. On the contrary, in the presence of copper complexes, olefin **II** was formed in amounts almost equal to those of the adduct at the early stages of reaction. Then, its yield passed through a maximum and, with a prolongation of the constant-temperature reaction, it decreased to 20–30% of the adduct yield (Fig. 1a). The long storage of samples at room temperature resulted in the virtually complete conversion of olefin **II** to the addition product **I**. In our opinion, such a reaction in the presence of, for example, binuclear phosphine complex occurs as a result of the interaction between the oxidized form of a catalyst and olefin. Thus, the formation and evolution of product **II** can be written as follows:

$$\mathrm{CH_2Cl{-}CH{=}CH_2 + CCl_4 + [L_{\mathit{n}}CuCl]_2} \longrightarrow \mathrm{CH_2{=}CH{-}CH_2{-}CCl_3 + [L_{\mathit{n}}CuCl]_2Cl_2},$$

$$\mathrm{CCl_3{-}CH_2{-}CH{=}CH_2 + [L_{\mathit{n}}CuCl]_2Cl_2} \longrightarrow \mathrm{CCl_3{-}CH_2{-}CHCl{-}CH_2Cl + [L_{\mathit{n}}CuCl]_2}.$$

The alternative mechanism implies the dechlorination of the addition product by the copper complex. This mechanism was reported for iron carbonyl complexes. We verified the possibilty of this mechanism by carrying out the reaction of 1,1,1,3,4-pentachlorobutane with the $[CuClPPh_3]_4$ complex at 403 K and found no olefin in the reaction products. Thus, the mechanism proposed by us for the formation of trichlorobutene appears to be the most probable.

The composition of products obtained in the presence of copper triphenylphosphine complexes was qualitatively identical to that obtained in the presence of monoethanolamine and dibutyl sulfide complexes. The kinetic curves of **I** and **II** accumulation obtained in the presence of dibutyl sulfide copper complexes are presented in Fig. 1. In the presence of the copper–DMF complex, as well as in the presence of benzoyl peroxide, the substitution products and hexachloroethane were observed along with the addition product. This points to the occurrence of the reaction mainly via the radical-chain mechanism.

Thus, the coordination mechanism of the reaction is operative in the presence of triphenylphosphine, monoethanolamine, and dibutyl sulfide complexes of copper. In the presence of these complexes, the reaction of CCl_4 with allyl chloride was much slower than with octene-1 and even with cyclohexane. This is clearly demonstrated by Fig. 1, where the accumulation curves for conversion products obtained under the same conditions in the reactions of cyclohexene and allyl chloride are presented (curves *4* and *5*). The measurable yields of the conversion products of allyl chloride were obtained in the presence of copper complexes only at 453 K. At the same time, it is known that, in the presence of radical initiators, the rate of allyl chloride conversion was 2.5 to 3 times higher than the rate of cyclohexene conversion [13]. Indeed, in our experiments, the extent of cyclohexene conversion in the presence of benzoyl peroxide was also ~20% (see Table 2), whereas the extent of allyl chloride conversion under similar conditions was higher than 60%.

It follows from Figs. 1 and 2 that the kinetics of the reaction of allyl chloride with CCl_4 is characterized by an induction period. Its length depends on many factors (the nature of ligand in the complex, the nuclearity of complex, the temperature, etc.). In our opinion, the induction period is related to the evolution of copper complexes. It is likely that, at the first stage of the reaction, immediately after mixing the reagents, an allyl-containing complex (**K**$_1$) that was inert in all possible mechanisms of the reaction was formed. Its formation follows from the above-mentioned low activity of the systems in the initiation of allyl chloride– CCl_4 interaction. If such a complex were not formed or if it initiated the process, allyl chloride, much like octene-1, could rapidly react via the radical-chain mechanism to give the addition product and it would be more active than cyclohexene at the initial stages of the reaction. It is likely that **K**$_1$ transformed further into a more active **K**$_2$ complex that was capable of initiating catalytic conversions by the coordination mechanism. At the same time, the binding of copper in this complex blocked the initiation of radical chains as before. Rather slow conversions of copper complexes into chlorinated olefin-containing polynuclear heterovalent structures were observed earlier in the isomerization of dichlorobutenes [11].

An important role of chlorinated olefin in the formation of **K**$_2$ complex was supported by the data on the effect of the pretreatment of initial complexes with allyl chloride in the absence of CCl_4. Earlier [8], we showed that the storage of these complexes in allyl chloride at 423 K for 1 h completely eliminated the induction period. The similarity to the isomerization of dichlorobutenes also manifested itself in the virtual independence of the reaction rate on the initial valence of copper; only the length of the induction period was dependent on it. The comparison of curves *2* and *4* in Fig. 2 showed that, at equal concentrations of reagents and components of the complex, the kinetic curves became parallel after the induction period. Such behavior was typical of the processes occurring over heterovalent polynuclear complexes [11].

The formation of Cu(II)-containing complexes in the presence of allyl chloride was confirmed by the electron spectroscopic data. After being kept at a constant temperature in the presence of allyl chloride or in the mixture of allyl chloride and CCl_4, the solutions of CuCl complexes of Bu_2S and PPh_3 turned yellow, and their electron spectra exhibited new bands at 380, 452, and 660 nm (for Bu_2S complexes, see Fig. 3) or at 380, 420, and 470 nm (for PPh_3 complexes, see [8]). Similar spectra were observed earlier for the CuCl–R_2S–dichlorobutene systems. The association of the latter spectra with the formation of polynuclear heterovalent complexes involving chlorinated olefin was proven by kinetic and spectroscopic data. It follows from Fig. 4 that, in the course of the reaction, the intensity of bands in the region of 400–500 nm passed through a maximum, and the time at which absorbance was maximal corresponded to the maximum reaction rate. When CCl_2 was used as the initial chloride, spectra were identical, the only difference being that the maximum intensity was attained virtually at once. Note that, in this case, the induction period was absent from kinetic curves. All the facts mentioned above allowed us to believe that an allyl-containing polynuclear complex was responsible for the occurrence of the reaction of allyl chloride with CCl_4. The heating of copper complexes in octene or cyclohexene insignificantly changed the spectra, induction periods for these olefins were not observed, and reaction products, as was shown above, corresponded to the radical process.

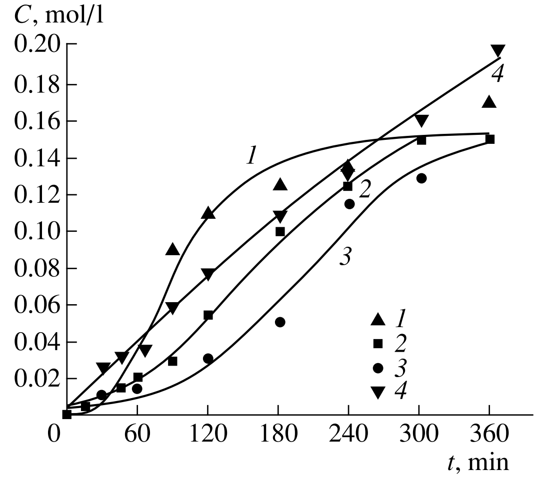

Fig. 2. Accumulation curves for the product of CCl_4 addition to allyl chloride in the presence of (*1*–*3*) CuCl or (*4*) $CuCl_2$ and (*1*) 0.24, (*2, 4*) 0.15, and (*3*) 0.08 M Bu_2S.

It might be assumed that the copper complex of a donor ligand and allyl chloride contained two strongly interacting Cu(II) ions. This followed from the comparison of electron and ESR spectra. The electron spectra pointed to the presence of Cu(II) (typical bands corresponding to the charge transfer from a ligand to metal and absorption in the region of *d*–*d* transitions) in the course of the reaction and after its completion. However, when CuCl was used as an initial copper chloride, the ESR spectrum was not observed at all; when $CuCl_2$ was the initial copper chloride, the intensity of the initial ESR signal decreased three and more times after the addition of allyl chloride. The observed picture was typical of systems in which formally diamagnetic complexes containing two or more Cu(II) ions are formed. The necessary component of such a complex is not only chlorinated olefin but an organic donor ligand as well. This was proven by the dependence of the catalytic activity on the presence of ligands. In the absence of ligands, CuCl($CuCl_2$)–chloroalkene–CCl_4 systems were virtually inert, and the electron spectra looked dif-

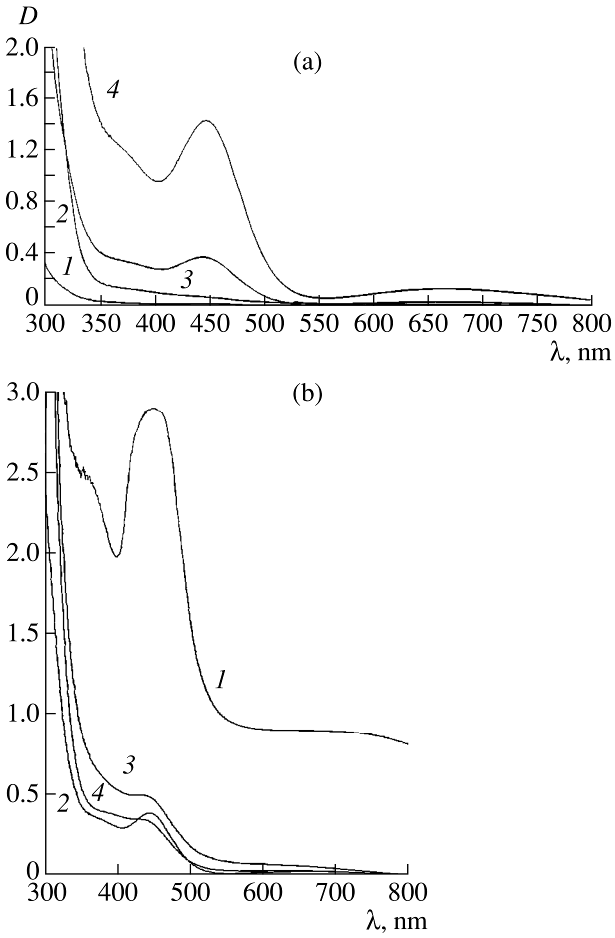

Fig. 3. Absorption spectra of CuCl–Bu_2S–allyl chloride–CCl_4 reaction solutions (a) after maintaining their temperature at 403 K for 1 h and at concentrations of Bu_2S of (*1*) 0, (*2*) 0.08, (*3*) 0.24, and (*4*) 0.64 M and (b) after maintaining their temperature at 403 K for (*1*) 0.5, (*2*) 1, (*3*) 3, (*4*) 5 h at $[Bu_2S] = 0.24$ M, [Cu] = 0.08 M, [Ol] = 0.9 M, and $[CCl_4] =$ 9.6 M.

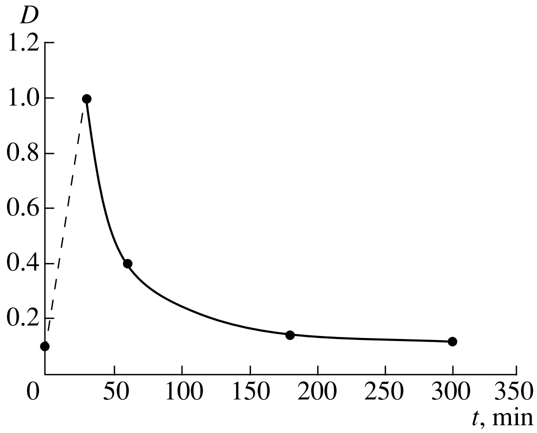

Fig. 4. Effect of the time of maintaining the temperature of CuCl–Bu_2S–allyl chloride–CCl_4 solutions at 403 K on absorbance at 450 nm ($[Bu_2S] = 0.24$ M, [Cu] = 0.08 M, [Ol] = 0.9 M, and $[CCl_4] = 9.6$ M).

ferent. It turned out that a decrease in the concentration of complexes and in their activity that was observed during the process when the extent of the reaction was higher than 30–40% was due to the consumption of ligands in side reactions. In prolonged reactions, ligands were oxidized to form disulfide and the corresponding chloroalkane in the case of Bu_2S and phosphine oxide or an analogous chlorinated derivate of phosphorus in the case of PPh_3. The repeated addition of a new portion of the donor (sulfide or phosphine) resulted in the complete restoration of the initial catalytic activity and in the formation of new portions of the product even in those samples where the reaction virtually ceased once the extent of the reaction reached 30–40%.

Our results support the assumption that the rate, products, and mechanism of the reaction of carbon tetrachloride with unsaturated hydrocarbons are governed to a great extent by the nature of these hydrocarbons. Depending on the nature of unsaturated hydrocarbons, we observe typical radical-chain reactions and radical processes that involve radicals bound in complexes or the processes that are formed via the coordination mechanism, most probably without the participation of free radicals.

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